

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-157914  
(43)Date of publication of application : 30.05.2003

(51)Int.Cl.

H01M 14/00

H01L 31/04

(21)Application number : 2001-358090

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(22)Date of filing : 22.11.2001

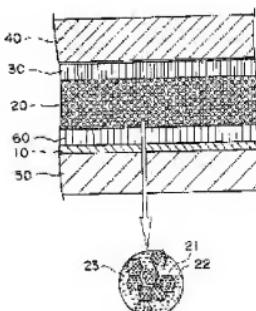
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(54) PHOTOELECTRIC CONVERSION ELEMENT, MANUFACTURING METHOD OF THE SAME, AND  
PHOTOCELL

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a photoelectric conversion element using semiconductor fine particle sensitized by pigment, having low cost, practical production aptitude, and excellent conversion efficiency and durability, and to provide a manufacturing method of the same, and a photocell using the same.

SOLUTION: The photoelectric conversion element has a conductive support on which, a semiconductor fine particle containing layer 20 containing semiconductor fine particle to which, pigment is adsorbed, an electric charge transport layer 30, and an opposing electrode 40. The electric charge transport layer 30 is made of gel electrolyte, and the opposing electrode 40 is made of conductive resin. The photocell uses the above photoelectric conversion element. The manufacturing method of the photoelectric conversion element includes an assembling process of sequentially laminating the semiconductor fine particle containing layer, the electric charge transport layer, and the opposing electrode.



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2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention]This invention relates to the photoelectric cell using an optoelectric transducer using the semiconductor particulate by which sensitization was carried out with coloring matter, a manufacturing method for the same, and this optoelectric transducer in detail about an optoelectric transducer, a manufacturing method for the same, and a photoelectric cell.

#### [0002]

[Description of the Prior Art]The optoelectric transducer is used for various kinds of photosensors, the copying machine, the optical power plant, etc. Various methods, such as what used metal, a thing using a semiconductor, a thing using an organic color or coloring matter, or a thing that combined these, are put in practical use by the optoelectric transducer.

[0003]A U.S. Pat. No. 4927721 item, said 4684537 No., said 5084365 No., Each specification of said 5350644 No., said 5463057 No., said 5525440 No., and WO 98/No. 50393, And the material and production technology for producing the optoelectric transducer (a "dye sensitizing optoelectric transducer" may be called hereafter.) using the semiconductor particulate by which sensitization was carried out to each gazette of JP,7-249790,A and Patent Publication Heisei No. 504521 [ ten to ] with coloring matter, or this are indicated. Since the advantage of this method can be used without refining cheap oxide semiconductors, such as a titanium dioxide, to a high grade, it is expected in that offer of a comparatively cheap optoelectric transducer is possible. However, such a dye sensitizing optoelectric transducer was expected the improvement highly [ endurance ] not necessarily enough.

[0004]On the other hand, although the liquid electrolyte which dissolved the redox kind in water or an organic solvent was used and high conversion efficiency is attained in the optoelectric transducer written for example, in the U.S. Pat. No. 4927721 item specification etc., There was a problem of photoelectric conversion efficiency not falling remarkably by evapotranspiration of an electrolysis solution and drain, if it is used over a long period of time, or stopping functioning as a cell.

[0005]In order to conquer such a fault, on WO 93/No. 20565 specifications. The optoelectric transducer using a solid electrolyte The Chemical Society of Japan, 7 (1997) 484 page, To JP,7-2881142,A, Solid State Ionics, 89 (1986) 263 page, and JP,9-27352,A, the optoelectric transducer solidified using the bridge construction polyethylene oxide system solid polymer electrolyte is indicated. However, it became clear that the optoelectric transducer using these solid electrolytes was in a level with insufficient photoelectric transfer characteristic especially short circuit current density, and endurance as a result of examination.

[0006]In WO 95/No. 18456 specification, the method of using as an electrolyte the imidazolium salt which is a low melting point compound is written as other means which prevent drain of an electrolysis solution and raise endurance. According to this method, since water and the organic solvent which were used as an electrolytic solvent can be conventionally managed with needlessness or a small quantity, endurance has been improved, but since it was liquid, there was concern of liquid leakage.

[0007]In order to prevent the above liquid leakage, the method of gelling an electrolyte and losing mobility is proposed. For example, the oil gelatinizing agent indicated to JP,2000-58140,A, Polymerization \*\*\*\* gelling of the monomer which has a nucleophilicity group of a statement in JP,2000-322932,A, and the monomer which has an electrophile nature group, "PolymerElectrolyte Revi ews-1 and 2" (J. R.MacCallum and C.A. Vincent) [ jointly and ] Polymer addition given in ELSEVIER APPLIED SCIENCE, The gelling by polymer and the cross linking agent which furthermore have a reactant group of a statement in JP,2000-86724,A, JP,2000-35550,A, JP,2001-160427,A, JP,2000-228234,A, etc., etc. are known.

[0008]After pouring in the liquid electrolyte before gelling in the gap of a semiconductor electrode layer and a conductive counter electrode board, the method of gelling with heat etc. is adopted as formation of the electrolyte layer using these gel electrolytes. However, in this method, in connection with the electrolytic capacity change or shape change by gelling, adhesion with a counter electrode side and an electrolyte is spoiled, and sufficient performance cannot be demonstrated. Also in a manufacturing process, there was a problem that the merit by which complicatedness is accompanied and which can be manufactured cheaply was spoiled.

#### [0009]

[Problem(s) to be Solved by the Invention]The purpose of this invention solves many problems in said former, and makes it a technical problem to attain the following purposes. That is, this invention has practical production aptitude, is cheap, and is

excellent in conversion efficiency and endurance, and an object of this invention is to provide the photoelectric cell using an optoelectric transducer using the semiconductor particulate by which sensitization was carried out with coloring matter, a manufacturing method for the same, and this optoelectric transducer.

[0010]

[Means for Solving the Problem] As a result of inquiring wholeheartedly in view of said technical problem, this invention persons find out that said purpose can be attained by charge transport layer which consists of gel electrolytes, and an optoelectric transducer which made conductive resin a counter electrode, and came to complete this invention. That is, said The means for solving a technical problem in this invention is as follows.

[0011] It is an optoelectric transducer, wherein it is an optoelectric transducer which has a semiconductor particulate contained layer, a charge transport layer, and a counterelectrode containing a semiconductor particulate which adsorbed coloring matter, said charge transport layer consists of gel electrolytes and said counterelectrode consists of conductive resin on <1> conductive substrate.

[0012]<2> Said gel electrolyte is an optoelectric transducer given in the above <1> which is the electrolyte gelled by the with a molecular weight of 1000 or less gelling agent.

[0013]<3> Said gel electrolyte is an optoelectric transducer given in the above <1> which is the electrolyte gelled by polymers gelling agent.

[0014]<4> Said gel electrolyte is an optoelectric transducer given in either of <3> from the above <1> as for which more than 60 mass % contains fused salt.

[0015]<5> Said gel electrolyte is an optoelectric transducer given in either of <4> from the above <1> containing a conductive particle.

[0016]<6> Said conductive resin is an optoelectric transducer given in either of <5> from the above <1> containing a conductive particle and a binder.

[0017]<7> It is an optoelectric transducer given in either of <6> from the above <1> in which it comes to laminate said charge transport layer and said counterelectrode.

[0018]<8> A semiconductor particulate contained in said semiconductor particulate contained layer is an optoelectric transducer given in either of <7> from the above <1> which contains a titanium dioxide at least.

[0019] It is a photoelectric cell which has an optoelectric transducer of a statement in either of <8> from <9> above <1>, and is characterized by things.

[0020] It is a manufacturing method of an optoelectric transducer having a process which laminates a semiconductor particulate contained layer containing a semiconductor particulate which adsorbed coloring matter, a charge transport layer which consists of gel electrolytes, and a counterelectrode, and it finishes setting up one by one on <10> conductive substrates.

[0021]<11> Manufacturing method of an optoelectric transducer given in the above <10> in which said counterelectrode consists of conductive resin.

[0022]

[Embodiment of the Invention] Hereafter, an optoelectric transducer of this invention, a manufacturing method for the same, and a photoelectric cell are explained in detail.

(An optoelectric transducer and a manufacturing method for the same) An optoelectric transducer of this invention and a manufacturing method for the same are explained first. It is an optoelectric transducer in which the optoelectric transducer of this invention has the semiconductor particulate contained layer, charge transport layer, and counterelectrode which contain the semiconductor particulate which adsorbed coloring matter on a conductive substrate, said charge transport layer consists of gel electrolytes, and said counterelectrode consists of conductive resin. In said optoelectric transducer, the cheap optoelectric transducer which the mode which comes to laminate said charge transport layer and said counterelectrode was preferred, and was excellent in the photoelectric transfer characteristic by that cause, and prevented degradation of the characteristic with the passage of time can be obtained. The manufacturing method of the optoelectric transducer of this invention has a process which laminates the semiconductor particulate contained layer containing the semiconductor particulate which adsorbed coloring matter, the charge transport layer which consists of gel electrolytes, and a counterelectrode, and it finishes setting up one by one on a conductive substrate.

[0023]<Gel electrolyte> In the optoelectric transducer of this invention, here explains the gel electrolyte which constitutes a charge transport layer. In this invention, the electrolyte in which the gel electrolyte which constitutes a charge transport layer contains a redox couple is gelled by the gelling agent. As this gelling agent, a with a molecular weight of 1000 or less gelling agent and a polymers gelling agent are used preferably. As for said gel electrolyte, what contains fused salt in more than 60 mass % is preferred, and its thing containing a conductive particle is preferred.

[0024]- As a redox couple contained in the electrolyte-electrolyte containing a redox couple, (a) I<sub>2</sub> and an iodide (metal iodides, such as LiI, NaI, KI, CsI, and CaI<sub>2</sub>.) Or combination with the iodine salt of the 4th class ammonium compounds, such as a tetraalkylammonium iodide, iodination pyridinium, and iodination imidazolium, (b) Br<sub>2</sub> and a bromide () [ LiBr, NaBr, KBr, CsBr and ] Metal bromide or tetra bromide alkylammonium, such as CaBr<sub>2</sub>, Combination with the bromine salt of the 4th class ammonium compounds, such as pyridinium bromide and bromination imidazolium, (c) Cl<sub>2</sub> and a chloride () [ LiCl, NaCl, KCl, CsCl and ] Metal chloride or tetra chloride alkylammonium, such as CaCl<sub>2</sub>, \*\*, such as sulfur compounds, such as combination with the chlorine salt of the 4th class ammonium compounds, such as pyridinium chloride and chloridation imidazolium, (d) sodium polysulfide, and alkyl thiol alkyl disulfide, (e) viologen coloring matter, and hydroquinone quinone,

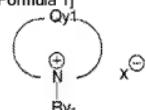
are mentioned suitably. Also in it, the combination of aforementioned (a)  $I_2$  and an iodide is preferred, and the combination of  $I_2$  and the iodine salt of the 4th class ammonium compound is more preferred. Said redox couple may be used by a 1-set independent, and 2 or more sets may be mixed and it may be used.

[0025]In the redox couple contained in an electrolyte, it is especially preferred to use fused salt also in said iodine salt from a viewpoint with which photoelectric conversion efficiency and endurance are compatible. Fused salt means a liquefied salt or the salt of a low melting point in a room temperature here. For example, pyridinium salt, imidazolium salt, a triazolium salt, etc. which are indicated to WO 95/No. 18456 specification, JP,8-259543,A, electrochemistry, the 65th volume, No. 11, 923 pages (1997), etc. can be mentioned. As for fused salt, what becomes liquefied in 100 \*\* or less, especially near a room temperature is preferred.

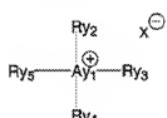
[0026]As fused salt which can be used preferably, the compound expressed by either following general formula (Y-a), (Y-b) and (Y-c) is mentioned.

[0027]

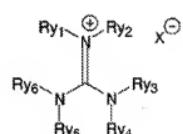
[Formula 1]



一般式 (Y-a)



一般式 (Y-b)



一般式 (Y-c)

[0028]In said general formula (Y-a), Qy1 expresses the atom group who can form the aromatic cation of 5 or 6 membered-rings with a nitrogen atom, and Ry1 expresses the alkyl group or alkenyl group which is not replaced [substitution or].

[0029]In said general formula (Y-b), it is preferred to be chosen from a group which consists of a carbon atom, a hydrogen atom, a nitrogen atom, an oxygen atom, and a sulfur atom as a composition atom of atom group Qy1 which can form an aromatic cation of 5 or 6 membered-rings with a nitrogen atom. As a five-membered ring formed in Qy1, An oxazole ring, a thiazole ring, an imidazole ring, a pyrazole ring, an isoxazole ring, A thiadiazole ring, an oxadiazole ring, a triazole ring, an indole ring, and a pyrrole ring are preferred, also in it, an oxazole ring, a thiazole ring, and an imidazole ring are more preferred, and an oxazole ring and especially an imidazole ring are preferred. As six membered-rings formed in Qy1, a pyridine ring, a pyrimidine ring, a pyridazine ring, a pyrazine ring, and a triazine ring are preferred, and a pyridine ring is more preferred.

[0030]In said general formula (Y-b), Ay1 expresses a nitrogen atom or a phosphorus atom, and Ry1, Ry2, Ry3, and Ry4 express an alkyl group or an alkenyl group which is not replaced [substitution or]. Two or more of Ry1, Ry2, Ry3, and Ry4 may form a non-aromatic ring which connects mutually and contains Ay1.

[0031]In said general formula (Y-c), Ry1, Ry2, Ry3, Ry4, Ry5, and Ry6 may express an alkyl group or an alkenyl group which is not replaced [substitution or], among those two or more may connect them mutually, and they may form a ring structure.

[0032]In said general formula (Y-a), (Y-b), and (Y-c), Ry1, Ry2, Ry3, Ry4, Ry5, and Ry6, it is an alkyl group (preferably, the numbers of carbon atoms are 1-24, and) which is not replaced [substitution or] independently respectively. May be straight

chain shape, branched state, or cyclic, and For example, a methyl group, An ethyl group, a propyl group, an isopropyl group, a pentyl group, a hexyl group, An octyl group, a 2-ethylhexyl group, t-octyl group, a decyl group, dodecyl, . A tetradecyl group, 2-hexyldecyl group, an octadecyl group, a cyclohexyl group, a cyclopentyl group, etc. are mentioned suitably. Or an alkenyl group (the numbers of carbon atoms may be 2-24 preferably, and it may be straight chain shape or branched state, for example, a vinyl group, an allyl group, etc. are mentioned suitably) which is not replaced [ substitution or ] is expressed. Also in it, an alkyl group whose numbers of carbon atoms are 2-18, and an alkenyl group whose numbers of carbon atoms are 2-18 are preferred, and especially an alkyl group whose numbers of carbon atoms are 2-6 is preferred.

[0033]In said general formula (Y-a), (Y-b), and (Y-c),  $Q_1$  and  $R_1$  -  $R_6$  may have a substituent, and as an example of a desirable substituent, halogen atoms (F, Cl, Br, I, etc.), a cyano group, and an alkoxy group (a methoxy group.) An ethoxy basis, a methoxyethoxy group, a methoxyethoxyethoxy basis, etc., aryloxy groups (phenoxy group etc.) and an alkylthio group (a methylthio group.) Alkoxy carbonyl groups, such as an ethyl thio group (ethoxycarbonyl group etc.), carbonic ester groups (ethoxycarbonyloxy group etc.) and an acyl group (an acetyl group.) Sulfonyl groups (a methane sulfonyl group.), such as a propionyl group and benzoyl Acyloxy groups, such as a benzenesulfonyl group (an acetoxy group, a benzoxyloxy group, etc.), A sulfonyloxy group (a methane sulfonyloxy group, a toluenesulfonyloxy group, etc.), phosphonyl groups (diethyl phosphonyl group etc.) and an amide group (an acetyl amine group.) Carbamoyl groups (N,N-dimethylcarbamoyl group etc.), such as a benzylamino group, an alkyl group (a methyl group, an ethyl group, a propyl group, an isopropyl group, a cyclopropyl group, a butyl group, a 2-carboxyethyl group, benzyl, etc.), Aryl groups (a phenyl group, a toluyl group, etc.), heterocycle groups (a pyridyl group, an imidazolyl group, a furanyl group, etc.), alkenyl groups (a vinyl group, 1-propenyl group, etc.), a silyl group, a silyloxy group, etc. are mentioned.

[0034]A compound expressed with said general formula (Y-a), (Y-b), and (Y-c) may form a polymer via  $Q_1$  or  $R_1$  -  $R_6$ .

[0035]A compound expressed with said general formula (Y-a), (Y-b), and (Y-c) may be used by an one-sort independent, or two or more sorts may use it, mixing. Although an iodine anion can be preferably used as a counter ion of fused salt expressed with  $X^-$ , it can also use together with fused salt which replaced an iodine anion with other anions. As an iodine anion and an anion to replace, Halide ion,  $SCN^-$  ( $Cl^-$ ,  $Br^-$ , etc.),  $BF_4^-$ ,  $PF_6^-$ ,  $ClO_4^-$ ,  $(CF_3SO_2)_2N^-$ ,  $2(CF_3CF_2SO_2)N^-$ ,  $CH_3SO_3^-$ ,  $CF_3SO_3^-$ ,  $CF_3COO^-$ ,  $Ph_4B^-$ ,  $3(CF_3SO_2)C^-$ , etc. are mentioned as a desirable example, It is more preferred that they are  $SCN^-$ ,  $CF_3SO_3^-$ ,  $CF_3COO^-$ ,  $2(CF_3SO_2)N^-$ , or  $BF_4^-$ . Alkali metal salt, such as other iodine salt, such as  $LiI$ ,  $CF_3COOLi$ ,  $CF_3COONa$ ,  $LiSCN$ , and  $NaSCN$ , can also be added. An addition of this alkali metal salt has a preferred 0.02 - 2 mass % grade, and its 0.1 - 1 mass % is more preferred.

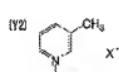
[0036]In a redox couple contained in an electrolyte, although an example of fused salt used preferably is given to below, this invention is not necessarily limited to these in any way.

[0037]

[Formula 2]



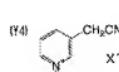
Y1-1  $X=I$   
Y1-2  $X=BF_4^-$   
Y1-3  $X=N(SO_2CF_3)_2$   
Y1-4  $X=PF_6^-$



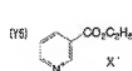
Y2-1  $X=I$   
Y2-2  $X=BF_4^-$   
Y2-3  $X=N(SO_2CF_3)_2$   
Y2-4  $X=CF_3SO_3^-$   
Y2-5  $X=SCN^-$



Y3-1  $X=I$   
Y3-2  $X=BF_4^-$   
Y3-3  $X=N(SO_2CF_3)_2$



Y4-1  $X=I$   
Y4-2  $X=BF_4^-$   
Y4-3  $X=N(SO_2CF_3)_2$

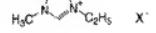


Y5-1  $X=I$   
Y5-2  $X=BF_4^-$   
Y5-3  $X=N(SO_2CF_3)_2$

[0038]

[Formula 3]

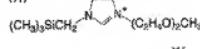
[Y8]



X'

Y8-1 X=I  
Y8-2 X=BF<sub>4</sub>  
Y8-3 X=N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>  
Y8-4 X=PF<sub>6</sub>

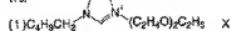
[Y7]



X'

Y7-1 X=I  
Y7-2 X=BF<sub>4</sub>  
Y7-3 X=N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>  
Y7-4 X=CF<sub>3</sub>COO  
Y7-5 X=SCN

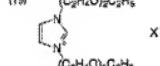
[Y8]



(1)C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> X'=I  
Y8-2 X=BF<sub>4</sub>  
Y8-3 X=N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>  
Y8-4 X=PF<sub>6</sub>

Y8-5 X=CF<sub>3</sub>COO  
Y8-6 X=SCN  
Y8-7 X=CF<sub>3</sub>SO<sub>3</sub>

[Y9]

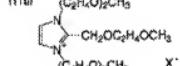


X'

(C<sub>2</sub>H<sub>4</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> X'=I  
Y9-2 X=BF<sub>4</sub>  
Y9-3 X=N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>  
Y9-4 X=CF<sub>3</sub>COO

Y9-5 X=SCN  
Y9-6 X=CF<sub>3</sub>SO<sub>3</sub>

[Y10]

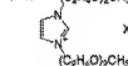


(C<sub>2</sub>H<sub>4</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> X'=I  
Y10-2 X=BF<sub>4</sub>  
Y10-3 X=N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>

[0039]

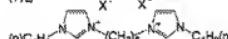
[Formula 4]

[Y11]



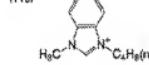
(C<sub>2</sub>H<sub>4</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> X'=I  
Y11-2 X=BF<sub>4</sub>  
Y11-3 X=N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>

[Y12]



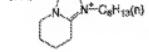
(n)C<sub>6</sub>H<sub>5</sub> X'=I  
Y12-2 X=BF<sub>4</sub>  
Y12-3 X=N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>

[Y13]



C<sub>6</sub>H<sub>5</sub>(n) X'=I  
Y13-2 X=BF<sub>4</sub>  
Y13-3 X=N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>

[Y14]



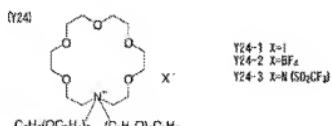
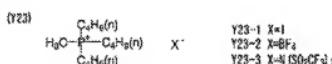
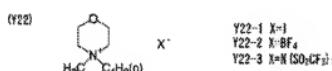
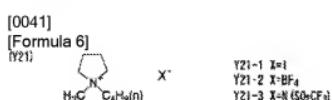
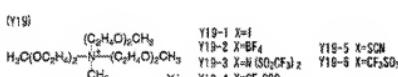
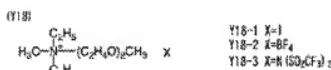
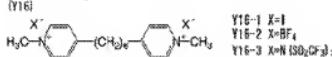
C<sub>6</sub>H<sub>10</sub>(n) X'=I  
Y14-2 X=BF<sub>4</sub>  
Y14-3 X=N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>

[Y15]

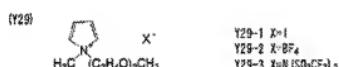
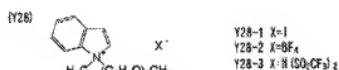
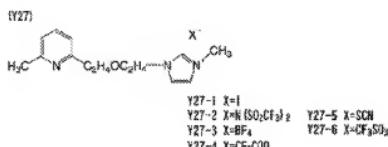
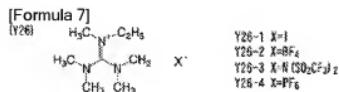


H<sub>3</sub>C-phenyl X'=I  
Y15-2 X=BF<sub>4</sub>  
Y15-3 X=N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>

[0040]  
[Formula 5]



[0042]



[0043]As for the fused salt contained in said electrolyte, what is a molten state at ordinary temperature is preferred, and it is preferred not to use a solvent. Although the solvent later mentioned to an electrolyte may be added, it is preferred that the content of fused salt is more than 60 mass % to the whole electrolyte, and it is preferred that it is especially more than 90 mass %. It is preferred that more than 50 mass % is iodine salt among fused salt.

[0044]It is preferred to add iodine, to said electrolyte, the content of iodine has [ as opposed to / the whole electrolyte / in this case ] preferred 0.1 - 20 mass %, and its 0.5 - 5 mass % is more preferred to it.

case J preferred 0.1 - 20 mass %, and its 0.5 - 5 mass % is more preferred to it.  
 [0045] As a solvent which can be added to said electrolyte, that whose viscosity can improve ionic mobility low, a thing of it being a compound which can reveal outstanding ion conductivity whose dielectric constant can improve effective-carriers concentration highly, etc. are preferred. As such a solvent, carbonate compounds, such as ethylene carbonate and propylene carbonate, Heterocyclic compounds, such as 3-methyl-2-oxazolidinone, dioxane, Ether compounds, such as diethylether, ethylene glycol dialkyl ether, Propylene glycol dialkyl ether, polyethylene-glycol dialkyl ether, Chain ether, such as polypropylene-glycol dialkyl ether, Methanol, ethanol, ethylene glycol monoalkyl ether, Propylene glycol monoalkyl ether, polyethylene-glycol monoalkyl ether, Alcohols, such as polypropylene-glycol monoalkyl ether, Ethylene glycol, propylene glycol, a polyethylene glycol, A polyhydric alcohol class of a polypropylene-glycol, glycerin, etc., acetonitrile, Aprotic polar substances, such as nitryl compounds, such as guru taro dinitrile, methoxy acetonitrile, propionitrile, and benzonitrile, dimethyl sulfoxide and sulfonyl water, etc. are mentioned usually, and these can also be mixed and used.

[0046] It is preferred to add basic compounds, such as J.Am.Ceram.Soc., *tert*-butylpyridine which is indicated to 80 (12) 3157-3171 (1997), 2-picoline, a 2,6-lutidine, to said electrolyte in this invention. A desirable density range in a case of adding a basic compound is below 2M (mol/L) more than 0.05M (mol/L).

[0047] In this invention, an electrolyte which added electric insulation particles, semiconductor particles, or/and a conductive particle can be used. In the case of electric insulation particles or semiconductor particles, a role of a spacer which separates semiconductor membrane and a counter electrode electrically is played. On the other hand, since a function of the counter electrode surface itself to supply an electrolyte with an electron when particles stand in a row from a counter electrode is achieved in the case of a conductive particle, an electrolyte layer (charge transport layer) is committed as an ion electronic conduction layer in this case. However, if semiconductor membrane and a counterelectrode (counter electrode) are short-circuited by use of this conductive particle, in order to start a depression, it is necessary to use so that it may not connect too hastily. As a size of these particles, 0.1 micrometer - 100 micrometers in diameter are preferred, and 0.5 micrometer - 30 micrometers are more preferred. As an addition to an electrolyte of these particles, 80 mass % - 2 mass % are preferred, and 50 mass % - 10 mass % are more preferred.

[0048]Arbitrary things will be used if it is a substance [ inertness / electrolyte ] as said electric insulation particle. There is an oxide as such a substance and either amorphous oxide glass or a crystalline oxide can be used. An example of desirable oxide glass is oxide glass containing at least a kind of element chosen from aluminum, silicon, boron, and Lynn. An aluminum oxide is mentioned as an example of a desirable crystalline oxide. Particles which consist of organic high polymers can also be used as electric insulation particles. As a charge of an organic high polymer material which forms particles.

polymethylmethacrylate, polyethylene, polystyrene, polypropylene, polyvinylidene-<sup>\*\*</sup> olate, etc. are mentioned suitably.

semiconductor and metal chalcogenide (for example, an oxide and a sulfide.) Compounds (for example, strontium titanate, titanic acid calcium, titanium sodium, barium titanate, potassium niobate, etc.) etc. which have a perovskite structure, such as a selenide, are mentioned suitably.

[0050] As said conductive particle, if it is a material [ inertness / electrolyte ] and is the material which supplies an electron promptly to an oxidizer in an electrolyte, arbitrary things can be used. As a desirable material provided with such character, Au, Pt, carbon (graphite, carbon black, acetylene black, corks, carbon fiber, a black lead carbon micro bead, etc.), aluminum, Pd, germanium, nickel, etc. can be mentioned. They may use them, using these by an one-sort independent, using two or more kinds together, and compounding making each support further etc. Particles which gave electron conductivity substantially to the surface of particles of electric insulation by plating Au and Pt, or particles which supported Pt selectively to an above-mentioned carbon particle (especially graphite), and have improved an electron transferring rate are used preferably. A foaming metal can also be used.

[0051]- In electrolytic gelling-this invention, as a gel electrolyte which constitutes a charge transport layer, It is producible by making an electrolyte containing said redox couple gel with the technique of \*\*, such as (i) oil gelatinizing agent addition, a polymerization containing (ii) polyfunctional monomer, (iii) polymer addition, and crosslinking reaction of (iv) polymer (solidification).

[0052](i) When making it gel by gelling oil gelatinizing agent addition by oil gelatinizing agent addition, J. Chem Soc.Japan, Ind.Chem.Sec., 46,779 (1943), J. Am.Chem.Soc., 111 and 5542 (1989), J.Chem.Soc., Chem.Commun., 1993 and 390, Angew.Chem.Int.Ed.Engl., 35, 1949 (1996). Although Chem.Lett., 1996 and 885, J.Chm.Soc., Chem.Commun., and a compound indicated to 1997 and 545 can be used, as a desirable compound, a compound which has amide structure is mentioned into molecular structure. An example to which an example which gelled an electrolysis solution gelled a fused salt electrolyte to JP,11-185863,A is indicated to JP,2000-58140,A, and can be preferably applied to this invention. As a molecular weight of these oil gelatinizing agents, it is preferred that it is 1000 or less, and it is more preferred that it is 500 or less. As an addition of a gelling agent, 40 - 0.1 mass % is preferred, and 5 - 1 mass % is still more preferred.

[0053](ii). Were indicated to gelling JP,2000-322932,A by polymerization containing polyfunctional monomer. A compound (A) which has two or more nucleophilicity groups (for example, nitrogen-containing heterocycle groups, such as an amino group, a pyridine ring, an imidazole ring, a thiazole ring, an oxazole ring, a triazole ring, a morpholine ring, a piperidine ring, and a piperazine ring), two or more electrophile nature groups (for example, alkyl halide and aralkyl halide.) Sulfonic ester, an acid anhydride, acid chloride, an isocyanate, alpha, A compound (B) which has beta-unsaturation sulfonyl group, alpha, beta-unsaturated carbonyl group, alpha, and beta-unsaturated nitrile group etc. can be made to be able to react, and a method of gelling by making a network by polymerization can also be used preferably. As a molecular weight of these compounds, 1000 or less are preferred and 500 or less are more preferred. As an addition of a compound (A), 20 - 0.1 mass % is preferred, and 5 - 1 mass % is more preferred. Quantity from which a functional group of a compound (B) becomes 3 mol equivalents to 0.1 mol equivalent to a reactant group of a compound (A) as an addition of a compound (B) is preferred, and quantity which turns into 1 mol equivalent to 0.3 mol equivalent is more preferred.

[0054](iii) When making it gel by gelling polymer addition by polymer addition, "Polymer Electrolyte Revi ews-1 and 2" (J. R.MacCallum and C.A.Vincent) [ jointly and ] A compound indicated to ELSEVIER APPLIEDSCIENCE can be used, for example, polymers gelling agents, such as polyacrylonitrile and polyvinylidene fluoride, are used especially suitably. As an addition of this polymer, 40 mass % - 0.1 mass % are preferred, and 10 mass % - 1 mass % are more preferred.

[0055](iv) When making an electrolyte gel by crosslinking reaction of gelling polymer by polymer crosslinking reaction, it is preferred to use an above-mentioned compound (B) together as polymer (C) containing a reactant group which can construct a bridge, and a cross linking agent. In this case, as a reactant group in which desirable bridge construction is possible, an amino group, nitrogen-containing heterocycles (for example, a pyridine ring, an imidazole ring, a thiazole ring, an oxazole ring, a triazole ring, a morpholine ring, a piperidine ring, a piperazine ring, etc.), etc. are mentioned. As a desirable cross linking agent, to a nitrogen atom, a reagent of two or more organic functions in which an electrophilic reaction is possible. It is for example, alkyl halide, aralkyl halide, sulfonic ester, acid anhydride, acid chloride, isocyanate, alpha, beta-unsaturation sulfonyl group, alpha, beta-unsaturated carbonyl group, alpha, and beta-unsaturated nitrile group etc. As an example of desirable polymer and a cross linking agent, it is indicated in JP,2000-86724,A, a 2000-35550 gazette, or a 2001-160427 gazette. A cross linking technique indicated in JP,2000-17076,A, a 2000-86724 gazette, a 2001-160427 gazette, and a 2000-228234 gazette is also applicable. An addition of polymer (C) has 20 mass % - preferred 0.1 mass %, and 10 mass % - 1 mass % are still more preferred. An addition of a cross linking agent (B) has a preferred quantity from which a functional group of a cross linking agent becomes 3 mol equivalents to 0.1 mol equivalent to a reactant group of polymer (C), and its quantity which turns into 0.3 mol equivalents from 1 mol equivalent is more preferred.

[0056](v) Formation of a formation gel electrolyte layer of a gel electrolyte layer is performed by making it gel, after applying to dye sensitizing semiconductor membrane an electrolytic solution which added a gelling agent stated to said electrolyte by said (i) - (iv) and making it permeate fine pores of semiconductor membrane. In a method of said (i) and (iii), after solvation-gelling is thermally reversible, heats an electrolyte, makes it a sol state and applies to semiconductor membrane, it gels by lowering to gelation temperature. Said (ii) and (iv) are methods gelled by crosslinking reaction, and after they apply an electrolyte before a reaction to semiconductor membrane, they gel with heating. Another or same gel electrolyte layer may be made to laminate on a gel electrolyte layer formed as mentioned above. Here, another gel electrolyte layer differs in an electrolytic presentation, or means that from which, and a kind of gelling agent and concentration differ. For example, it is possible to laminate a gel electrolyte containing said conductive particle on a gel electrolyte which does not contain a conductive particle, and to improve electronic contact with a counter electrode. A gel electrolyte layer where cross linking

agent concentration is high can be made to form in disadvantageous semiconductor membrane for ion transport ability at a side near a counter electrode as which a mechanical strength is required using gel with low cross linking agent concentration. After infiltrating into semiconductor membrane an electrolyte which does not contain a gelling agent, a gel electrolyte layer may be formed from on the.

[0057]A counterelectrode which an optoelectric transducer of <conductive resin> this invention has will not be limited especially if it is resin in which conductivity is shown. Conductive resin which may use a thing as shows conductivity by sole resin like poly aniline, and contains a conductive particle and a binder may be sufficient as it. For example, conductive resin of said conductive particle content, A binder distributes a conductive particle, it dilutes with an organic solvent preferably, what can be applied is meant, and it is called a conductive paint, electroconductive glue, or conductive paste, and is widely used as a special paint and adhesives for electronics. In this invention, as a conductive particle used preferably, a conductive particle mentioned above in said electrolyte composition is mentioned, and carbon, Pt, etc. are suitably mentioned as a desirable material also in it.

[0058]A role of said binder connects particles with a chain, gives conductivity, and are physical and a thing of a conducting film which gives chemical stability further at the same time it sticks a conductive particle to a substrate. There are a paint type and an adhesives type and these are further divided into a high-temperature-firing type, a cold cure dry type, and an ultraviolet curing type according to curing conditions by the characteristic of a binder to be used. As a binder used preferably, acrylic resin (room-temperature-setting type 1 liquid type), Hardening agents (heat-hardened type), such as epoxy system resin, an amino system hardening agent (room-temperature-setting type 1 liquid type), phenol system resin, an epoxy resin and urethane resin, dicyandiamide, a boron trifluoride amine complex, and imidazole, etc. are mentioned suitably. Also in it, epoxy system resin and especially phenol system resin are preferred.

[0059]As an organic solvent used for dilution, an existing thing of solubility over resin is chosen according to a kind of binder. When applying to a gel electrolyte layer directly, it is preferred to choose polar comparatively low solvents, such as a gel electrolyte layer and toluene which is hard to dissolve.

[0060]A gel electrolyte (charge transport layer) in which a <lamination> organic solvent is not contained, or an organic solvent content is low, and fused salt occupies more than 80 mass %, Since compatibility with polar comparatively low organic solvents, such as ethyl acetate and toluene, is low, it is possible to make conductive resin (counterelectrode) apply and laminate directly on these gel electrolytes (charge transport layer). When applying conductive resin, it may dilute with ester solvents, such as hydrocarbon system solvents, such as toluene, and ethyl acetate, if needed. After spreading can distill off a solvent, can harden it by a method according to resin, and can make a counter electrode (counterelectrode) layer form. As long as material used at the time of lamination of the above gel electrolyte and counterelectrode so that degradation may not be started is chosen, a method of acting as Hitoshi of two or more layers collectively can also be performed. By using an electrolyte layer using a gel electrolyte of this invention, the former, After pouring a liquid electrolyte before gelling into a gap of a semiconductor electrode layer and a conductive counter electrode board, compared with a method of gelling this with heat etc., adhesion with a counter electrode side and an electrolyte accompanying an electrolytic capacity change and a shape change by gelling is maintained. Also in a manufacturing process, since a simple method of finishing setting up each class one by one can be taken and also it becomes easy [ large-area-izing ], a merit which can be manufactured cheaply is fully enjoyable.

[0061]<composition of an optoelectric transducer, and material> -- here, the composition and material are explained about an optoelectric transducer of this invention. An optoelectric transducer of this invention has a semiconductor particulate contained layer, a charge transport layer, and a counterelectrode which contain a semiconductor particulate which adsorbed coloring matter on a conductive substrate, said charge transport layer consists of gel electrolytes, and said counterelectrode consists of conductive resin. An optoelectric transducer of this invention is manufactured by laminating a semiconductor particulate contained layer containing a semiconductor particulate which adsorbed coloring matter, a charge transport layer which consists of gel electrolytes, and a counterelectrode, and finishing setting up one by one on a conductive substrate. It laminates in order of the conductive layer 10, the under coat 60, the photosensitive layer (semiconductor particulate contained layer) 20, the gel electrolyte layer (charge transport layer) 30, and the counter electrode conductive layer (counterelectrode) 40, and an optoelectric transducer of this invention becomes, as preferably shown in drawing 1. Said photosensitive layer (semiconductor particulate contained layer) 20 comprises the semiconductor particulate 21 by which sensitization was carried out with the coloring matter 22, and the gel electrolyte material (charge transporting material) 23 which permeated an opening between these semiconductor particulates 21. The gel electrolyte material (charge transporting material) 23 consists of the same ingredient as material used for the gel electrolyte layer (charge transport layer) 30. In order to give intensity to an optoelectric transducer of this invention, the substrate 50 may be formed as a ground of the conductive layer 10 and/or the counter electrode conductive layer (counterelectrode) 40. Hereafter, in this invention, a layer which consists of the conductive layer 10 and the substrate 50 which it is arbitrary and is formed is called a "conductive substrate." It is the photoelectric cell which was made in order to connect this optoelectric transducer to external load and to do electric work (power generation), and it is the photosensor which was made for the purpose of sensing of optical information. A case where call a "photoelectrochemical cell" especially a case where the gel electrolyte material (charge transporting material) 23 mainly consists of ion transport material among photoelectric cells, and power generation by sunlight is made into a key objective is called a "solar cell."

[0062]When a semiconductor particulate is a n type in an optoelectric transducer of this invention shown in drawing 1, Coloring matter 22 grade is excited, an electron of high energy in excited coloring matter 22 grade is passed to a conducting zone of the semiconductor particulate 21, and light which entered into the photosensitive layer (semiconductor particulate

contained layer) 20 containing the semiconductor particulate 21 by which sensitization was carried out with the coloring matter 22 reaches the conductive layer 10 by diffusion further. At this time, a molecule of coloring matter 22 grade serves as an oxidant. In a photoelectric cell, while an electron in the conductive layer 10 works in an external circuit, through the counter electrode conductive layer (counterelectrode) 40 and the gel electrolyte layer (charge transport layer) 30, it returns to an oxidant of coloring matter 22 grade, and the coloring matter 22 is reproduced. The photosensitive layer (semiconductor particulate contained layer) 20 works as a negative electrode (optical anode), and commits the counter electrode conductive layer (counterelectrode) 40 as an anode. A boundary of each layer [For example, a boundary of the conductive layer 10 and the photosensitive layer (semiconductor particulate contained layer) 20, On a boundary of the photosensitive layer (semiconductor particulate contained layer) 20 and the gel electrolyte layer (charge transport layer) 30, and a boundary of the gel electrolyte layer (charge transport layer) 30 and the counter electrode conductive layer (counterelectrode) 40], the constituents of each class may be carrying out diffusive mixing mutually. Each class is explained in detail below.

[0063]- A conductive substrate-conductive substrate may serve as a case where it consists of a monolayer of a (i) conductive layer from a (ii) conductive layer and two-layer [ of a substrate ]. In said (i), as a conductive layer, material that intensity and sealing performance are fully maintained is used, for example, a metallic material (alloys containing these, such as platinum, gold, silver, copper, zinc, titanium, and aluminum) can be used. In said (ii), a substrate which has a conductive layer which contains a conducting agent in the photosensitive layer side can be used, as a desirable conducting agent - metal (for example, platinum, gold, silver, copper, and zinc.) An alloy containing these and carbon, such as titanium, aluminum, and indium, conductive metallic oxide (what doped fluoride or antimony to an indium tin multiple oxide and tin oxide), etc. are mentioned suitably. As thickness of a conductive layer, about 0.02-10 micrometers is preferred.

[0064]A conductive substrate is so good that surface resistance is low. The range of desirable surface resistance is below 50ohms / \*\*, and is below 20ohms / \*\* still more preferably.

[0065]As for a conductive substrate, when irradiating with light from the conductive substrate side, it is preferred that it is substantially transparent. That it is transparent means substantially that transmissivity is not less than 10% in some or the whole region of light of a visible - near infrared region (400-1200 nm), it is preferred that it is not less than 50%, and not less than 80% is more preferred. It is preferred that transmissivity of a wavelength band where a photosensitive layer has sensitivity especially is high.

[0066]What formed a transparent conductive layer which consists of conductive metallic oxide in the surface of transparent substrates, such as glass or a plastic, by spreading or vacuum evaporation as a transparent conductive base material is preferred. A thing desirable as said transparent conductive layer is diacid-ized tin which doped fluoride or antimony, or an indium tin oxidation thing (ITO). A transparent polymer film besides glass substrates, such as advantageous soda glass and alkali free glass without influence of alkaline elution, can be used for said transparent substrate from a viewpoint of low cost and intensity. As a material of a transparent polymer film, triacetyl cellulose (TAC), Polyethylene terephthalate (PET), polyethylenenaphthalate (PEN), Syndiotactic poly styrene (SPS), a polyphenylene sulfide (PPS), There are polycarbonate (PC), polycarbonate (PA), polysulfone (PSF), polyester sulfone (PES), polyimide (PI), polyether imide (PEI), cyclic polyolefin, bromine-ized phenoxy, etc. In order to secure sufficient transparency, as coverage of conductive metallic oxide, it is preferred to be referred to per base material 1m<sup>2</sup> of glass or a plastic and as 0.01-100g.

[0067]It is preferred to use a metal lead in order to lower resistance of a transparent conductive base material. As construction material of a metal lead, metal, such as platinum, gold, nickel, titanium, aluminum, copper, and silver, is preferred. As for a metal lead, it is preferred to install in a transparent substrate by vacuum evaporation, sputtering, etc., and to provide on it a transparent conductive layer which consists of conductive tin oxide or an ITO film. A fall of incident light quantity by metal lead installation is 1 to 5% more preferably less than 10%.

[0068]- A photosensitive layer (semiconductor particulate contained layer)-photosensitive layer (semiconductor particulate contained layer) comprises a semiconductor particulate by which sensitization was carried out with coloring matter, and gel electrolyte material (charge transporting material) which permeated an opening between these semiconductor particulates. In said photosensitive layer, a semiconductor acts as a photo conductor, absorbs light, performs charge separation, and produces an electron and an electron hole. In a semiconductor by which dye sensitizing was carried out, generating of optical absorption, an electron by this, and an electron hole takes place mainly in coloring matter, and a semiconductor receives this electron (or electron hole), and bears a role to transmit. It is preferred that it is an n-type semiconductor which gives anode current by a conductor electron serving as a carrier under optical pumping as a semiconductor used by this invention.

[0069](i) An element semiconductor like silicon and germanium as a semiconductor semiconductor, chalcogenide (for example, an oxide.) of an III-V system compound semiconductor and metal Compounds (for example, strontium titanate, titanic acid calcium, titanium sodium, barium titanate, potassium niobate, etc.) etc. which have a perovskite structure, such as a sulfide, selenides, or those composites, can be used.

[0070]As chalcogenide of desirable metal, titanium, tin, zinc, iron, Tungsten, a zirconium, hafnium, strontium, indium, An oxide of cerium, yttrium, a lanthanum, vanadium, niobium, or tantalum, cadmium, zinc, lead, silver, antimony or a sulfide of bismuth, cadmium or a leaden selenide, a telluride of cadmium, etc. are mentioned suitably. As other compound semiconductors, a selenide of phosphides, such as zinc, gallium, indium, and cadmium, gallium arsenide, or copper-indium, a sulfide of copper-indium, etc. are mentioned. A composite like  $M_xOyS_z$  or  $M_1xM_2yO_z$  (the number of combination whose valences M, M<sub>1</sub>, and M<sub>2</sub> become a metallic element, and, as for oxygen, x, y, and z, become [ O ] neutrality, respectively) can also be used preferably.

[0071]As a desirable example of a semiconductor used for this invention, Si, TiO<sub>2</sub>, SnO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, ZnO, Nb<sub>2</sub>O<sub>5</sub>,

CdS, ZnS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CdSe, CdTe, SrTiO<sub>3</sub>, GaP, InP, GaAs, CuInS<sub>2</sub>, CuInSe<sub>2</sub>, etc. are mentioned. Also in it, TiO<sub>2</sub>, ZnO, Sn<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, CdS, PbS, CdSe, SrTiO<sub>3</sub>, InP, GaAs, CuInS<sub>2</sub>, or CuInSe<sub>2</sub> is more preferred, TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> is still more preferred, and TiO<sub>2</sub> is the most preferred. As TiO<sub>2</sub>, TiO<sub>2</sub> which includes an anatase type crystal not less than 70% is preferred, and especially TiO<sub>2</sub> of a 100% anatase type crystal is preferred. It is the purpose of raising electronic conductivity in these semiconductors, and it is also effective to dope metal. As metal to dope, divalent and trivalent metal is preferred. It is the purpose of preventing a reverse current from flowing into a charge transport layer from a semiconductor, and it is also effective to dope univalent metal to a semiconductor.

[0072]As a semiconductor used for this invention, although a single crystal or polycrystal may be sufficient, viewpoints of a manufacturing cost, raw-material reservation, an energy payback time, etc. to polycrystal is preferred, and especially a porous membrane that consists of semiconductor particulates is preferred. An amorphous portion may be included in part.

[0073]As particle diameter of a semiconductor particulate, although it is generally an order of nm-mu m, as mean particle diameter of a primary particle for which it is asked from a diameter when a project area was converted into a circle, 5-200 nm is preferred and 8-100 nm is more preferred. As mean particle diameter of a semiconductor particulate (aggregated particle) in dispersion liquid, 0.01-30 micrometers is preferred. Two or more kinds of particles from which particle size distribution differs may be mixed, as for average size of small particles, 25 nm or less is preferred in this case, and 10 nm or less is more preferred. Particle diameter is big, for example, it is also preferred to mix a semiconductor particle (not less than 100 nm and about 300 nm) in order to scatter incident light and to raise an optical capturing rate on the other hand.

[0074]Semiconductor particulates may be two or more sorts of mixing from which it may use by an one-sort independent, and a kind of semiconductor particulate differs. As for one sort, when mixing and using two or more sorts of semiconductor particulates, it is preferred that they are TiO<sub>2</sub>, ZnO, Nb<sub>2</sub>O<sub>5</sub>, or SrTiO<sub>3</sub>. It is preferred that they are SnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> and WO<sub>3</sub> as one more sort. As a still more desirable combination, combination of \*\*, such as ZnO, SnO<sub>2</sub> and ZnO, WO<sub>3</sub> and ZnO or SnO<sub>2</sub>, and WO<sub>3</sub>, can be mentioned. When mixing and using two or more sorts of semiconductor particulates, each particle diameter may differ. Particle diameter of a semiconductor particulate especially quoted at the one above-mentioned item is large, and combination with small particle diameter of a semiconductor particulate quoted henceforth [ 2 items ] is preferred. Particles of particle diameter in which particles of large particle diameter are small at not less than 100 nm have especially a preferred combination of 15 nm or less.

[0075]As a method of producing a semiconductor particulate, Sumio Sakuhana's company of the "science of sol-gel method" AGUNE \*\* style (1998). A sol-gel method given in "thin-layer-coating art by a sol-gel method" (1995), etc. of TECHNICAL INFORMATION INSTITUTE, "composition of a monodisperse particle by the new synthetic method gel -\*\*\*\* method and size gestalt control" of Tadao Sugimoto - wait -- \*\*\*\*, the 35th volume, No. 9, and the gel -\*\*\*\* method of a 1012-1018 pages (1996) statement are preferred. A method of producing an oxide for a chloride which Degussa developed by elevated-temperature hydrolysis in an acid water matter salt is also preferred.

[0076]When a semiconductor particulate is titanium oxide, each of above-mentioned sol-gel methods, gel -\*\*\*\* methods, and elevated-temperature hydrolysis methods in inside of an acid water matter salt of a chloride is preferred, but a sulfuric acid method and a chlorine method of a statement can also be further used for Manabu Seino's "titanium oxide physical-properties and applied-technology" Gihodo Shuppan (1997). Furthermore, as a sol-gel method, a method of a journal OBU American ceramic society of Barbe and others, the 80th volume, No. 12, and a 3157-3171 pages (1997) statement, A method of chemistry OBU MATERIARUZU of Burnside and others, the 10th volume, No. 9, and a 2419-2425-page statement is also preferred.

[0077](ii) In order to apply a formation semiconductor particulate of a photosensitive layer (semiconductor particulate contained layer) on a conductive substrate, the above-mentioned sol-gel method other than a method of applying dispersion liquid or a colloidal solution of a semiconductor particulate on a conductive substrate, etc. can also be used. When fertilization of an optoelectric transducer, the physical properties of semiconductor particulate liquid, the flexibility of a conductive substrate, etc. are taken into consideration, a wet film production method is comparatively advantageous. As the wet film production method, the applying method, print processes, an electrolytic deposition method, and an electrodeposition process are typical. A method of oxidizing metal, a method (the LPD method) of depositing in the liquid phase by ligand exchange etc. from a metal solution, a method of vapor-depositing by weld slag etc., a CVD method, or the SPD method that sprays a metallic-oxide precursor which carries out a pyrolysis, and forms a metallic oxide on a warmed substrate can also be used.

[0078]When compounding a method of distributing while grinding as a method of producing dispersion liquid of a semiconductor particulate using a method and a mill which are mashed with a mortar other than the above-mentioned sol-gel method, or a semiconductor, a method of depositing as particles and using it as it is in a solvent, etc. are mentioned.

[0079]As carrier fluid, water or various kinds of organic solvents (for example, methanol, ethanol, isopropyl alcohol, citronellol, terpineol, dichloromethane, acetone, acetonitrile, ethyl acetate, etc.) are mentioned suitably. In the case of distribution, polymer like a polyethylene glycol, hydroxyethyl cellulose, and carboxymethyl cellulose, a surface-active agent, acid, or a chelating agent may be used as a distributed auxiliary agent if needed. Since a semiconductor particulate contained layer which regulation of viscosity of dispersion liquid is attained and does not separate further easily due to changing a molecular weight of a polyethylene glycol can be formed or voidage of a semiconductor particulate contained layer can be controlled, it is preferred to add a polyethylene glycol.

[0080]As a coating method, the air knife method, the braid method, etc. the roller method, a dip method, etc. as a meter ring system as an application system as that where application and a meter ring are made at identical parts, The slide hopper

method given in each specification (the wire bar method currently indicated by JP,58-4589,B, U.S. Pat. No. 2681294 No., said 2761419 No., and the 2761791 No.), the extrusion method, the curtain method, etc. are preferred. Spin method and a spray method are also preferred as a general aviation. As a wet printing method, letterpress, offset, and the three major print processes of photogravure are begun, and an intaglio, a rubber plate, screen-stencil, etc. are preferred. According to liquid viscosity or wet thickness, a desirable film production method is chosen from these.

[0081] The semiconductor particulate contained layer can carry out multilayer spreading of the dispersion liquid of a semiconductor particulate with which not only a monolayer but particle diameter is different, or can also carry out multilayer spreading of the coating layer containing a semiconductor particulate (or a different binder, an additive agent) from which a kind differs. Also when thickness is insufficient, multilayer spreading is effective at one-time spreading.

[0082] Since support pigment quantity per unit project area increases, a capturing rate of light becomes high so that thickness (it is the same as thickness of a photosensitive layer) of a semiconductor particulate contained layer generally becomes thick, but a loss by electric charge recombination whose generated diffusion length of electron increases simultaneously also becomes large. Therefore, as desirable thickness of a semiconductor particulate contained layer, it is 0.1-100 micrometers. When using for a photoelectric cell, as thickness of a semiconductor particulate contained layer, 1-30 micrometers is preferred and 2-25 micrometers is more preferred. Per base material 1m<sup>2</sup> of a semiconductor particulate, and as coverage, 0.5-100g are preferred, and 3-50g are more preferred.

[0083] Heat-treating is preferred, in order to raise improvement in film strength, and adhesion with a base material while contacting semiconductor particulates electronically after applying a semiconductor particulate on a conductive substrate. As a range of cooking temperature, not less than 40 \*\* 700 \*\* or less is preferred, and not less than 100 \*\* 600 \*\* or less is more preferred. As cooking time, 10 minutes - about 10 hours are preferred. Like a polymer film, when using a low base material of the melting point or softening temperature, high temperature processing is not preferred in order to cause degradation of a base material. As for cooking temperature, also from a viewpoint of cost, it is preferred that it is low temperature (for example, 50 \*\* - 350 \*\*) as much as possible. Low temperature-ization can also be performed by becoming possible by a small semiconductor particulate of 5 nm or less, heat-treatment under existence of mineral acid and a metallic-oxide precursor, etc., and impressing an exposure of ultraviolet rays, infrared rays, microwave, etc., an electric field, and an ultrasonic wave. It is preferred to use together, combining suitably the above-mentioned exposure, heating besides impression, decompression, oxygen plasma treatment, pure water washing, solvent cleaning, gas scrubbing, etc. In order to remove an unnecessary organic matter etc. simultaneously.

[0084] It is the purpose of increasing surface area of a semiconductor particulate, or raising purity near the semiconductor particulate after heat-treatment, and raising electron injection efficiency from coloring matter to a semiconductor particulate, and electrochemical plating treatment using chemical-plating processing and titanium trichloride solution using a titanium tetrachloride aqueous solution may be performed, for example. It is the purpose of preventing a reverse current from flowing into a charge transport layer from a semiconductor particulate, and it is effective to also make low organic matters of electronic conductivity other than coloring matter stick to a particle surface. What has a hydrophobic radical as an organic matter made to adsorb is preferred.

[0085] As for a semiconductor particulate contained layer, it is preferred to have large surface area so that much coloring matter can be adsorbed. As for surface area in the state where a layer of a semiconductor particulate was applied on a base material, 10 or more times is preferred to a project area, and its further 100 or more times are preferred. Although this maximum does not have restriction in particular, they are usually about 1000 times.

[0086](iii) It has absorption in a visible range or a near-infrared region, as sensitizing dye used for a coloring matter photosensitive layer (semiconductor particulate contained layer), if it is a compound which can carry out sensitization of the semiconductor, it can use arbitrarily, but organometallic complex coloring matter, methine coloring matter, porphyrin system coloring matter, and phthalocyanine system coloring matter are preferred especially. Since a wavelength band of photoelectric conversion is made large as much as possible and conversion efficiency is raised, two or more kinds of coloring matter can be used together or mixed. In this case, coloring matter used together or mixed and its rate can be chosen so that it may double with target wavelength band and intensity distribution of a light source.

[0087] As for such coloring matter, it is preferred to have the suitable bond groups (interlocking group) which has adsorption capability to the surface of a semiconductor particulate. An acidic group like a COOH group, an OH radical, an SO<sub>3</sub>H basis, a -P(O) (OH) 2 group, or a -OP(O) (OH) 2 group as this bond groups, Or a chelation group which has pi conductivity like oxime, dioxime, hydroxyquinoline, salicylate, or an alpha-ketoeno rate is mentioned suitably. Also in it, a COOH group, a -P(O) (OH) 2 group, and especially a -OP(O) (OH) 2 group are preferred. These bases may form an alkaline metal etc. and a salt, and may form inner salt. If an acidic group is contained like [ in case a methine chain forms a squarylium ring and a crocodile NIUMU ring ] in the case of poly methine coloring matter, it will be good also considering this portion as bond groups.

[0088] Desirable sensitizing dye used for a photosensitive layer (semiconductor particulate contained layer) is explained concretely hereafter.

(a) When organometallic complex pigment color matter is metal complex coloring matter, metal-phthalocyanines coloring matter, metalloporphyrin coloring matter, or ruthenium complex coloring matter is preferred, and especially ruthenium complex coloring matter is preferred. As ruthenium complex coloring matter, for example A U.S. Pat. No. 4927721 item, Said 4684537 No., said 5084365 No., said 5350644 No., said 5463057 No., A complex pigment of a statement is mentioned to the each specification [ of No. 5525440 ], JP,7-249790,A, and Patent Publication Heisei No. 504512 [ ten to ] gazette, WO 98/No. 50393 specification, JP,2000-26487,A, etc.

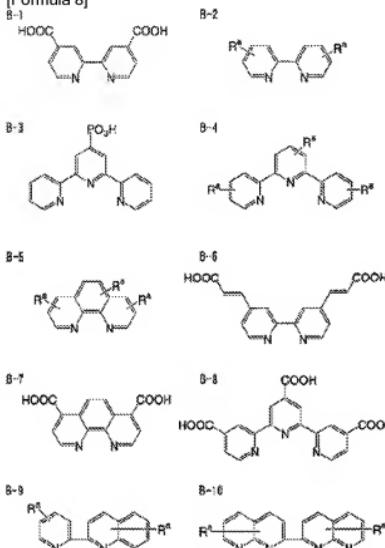
[0089] As ruthenium complex coloring matter furthermore used by this invention, what is expressed by following general formula (I) is preferred.

General-formula (I): (A<sub>1</sub>) pRu (B-a) (B-b) (B-c)

In said general formula (I), A<sub>1</sub> has a preferred ligand chosen from a group which expresses a ligand of 1 or 2 seats and consists of a derivative of Cl, SCN, H<sub>2</sub>O, Br, I, CN, NCO, SeCN and alpha-diketones, oxalic acid, and dithiocarbamic acid. p expresses an integer of 0-3. B-a, B-b, and B-c express respectively an organic ligand shown by a following formula (B-1) and either - (B-10) independently.

[0090]

[Formula 8]



[0091] In said formula (B-1) - (B-10), R<sup>a</sup> expresses a hydrogen atom or a substituent and as this substituent, For example, the alkyl group which is not replaced [ substitution with a halogen atom and 1-12 carbon atoms or ], The aryl group which is not replaced [ substitution with the aralkyl group which is not replaced / substitution with 7-12 carbon atoms or / and 6-12 carbon atoms or ], or an above-mentioned acidic group (the acidic group of these may form the salt) and chelation group are mentioned. Straight chain shape or branched state may be sufficient as the alkyl part in said alkyl group and an aralkyl group, and a monocycle or polycyclic (a condensed ring, a ring set) may be sufficient as the aryl portions of said aryl group and an aralkyl group. In said general formula (I), (B-a), (B-b), and (B-c) may be the same, or may differ from each other, and any one or two may be sufficient as them.

[0092] Although the desirable example (illustration compound R-1-17) of organometallic complex coloring matter is shown below, the coloring matter used for this invention is not limited to the following examples.

[0093]

[Formula 9]

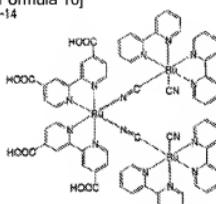
(A<sup>1</sup>)<sub>2</sub>Ru(B-a)(B-b)(B-c)

	A <sup>1</sup>	B	B-a	B-b	B-c	R*
R-1	SCN	2	B-1	B-1	—	—
R-2	CN	2	B-1	B-1	—	—
R-3	Cl	1	B-1	B-1	—	—
R-4	CH	2	B-7	B-7	—	—
R-5	SCN	?	B-7	B-7	—	—
R-6	SCN	3	B-1	B-2	—	H
R-7	SCN	1	B-1	B-3	—	—
R-8	Cl	1	B-1	B-4	—	H
R-9	I	2	B-1	B-5	—	H
R-10	SCN	3	B-8	—	—	—
R-11	CH	3	B-8	—	...	—
R-12	SCN	1	B-2	B-8	—	H
R-13	—	3	B-1	H-1	B-1	—

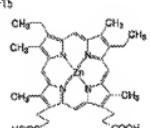
[0094]

[Formula 10]

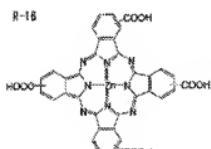
R-14



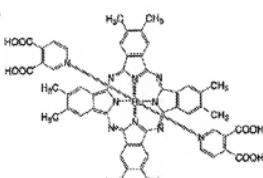
R-15



R-16



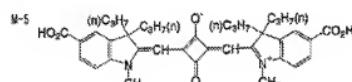
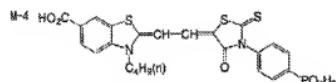
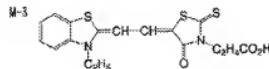
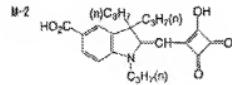
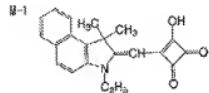
R-17



[0095](b) The desirable methine coloring matter used for methine coloring matter this invention is poly methine coloring matter, such as cyanine dye, merocyanine dye, and SUKUWARIRIUMU coloring matter. As poly methine coloring matter preferably used by this invention, For example, JP,11-35836,A, JP,11-67285,A, JP,11-86916,A,JP,11-97725,A, JP,11-158395,A, JP,11-163378,A, The coloring matter of a statement is mentioned in each specification (each gazette of JP,11-214730,A, JP,11-214731,A, JP,11-238905,A, and JP,2000-26487,A and European patent No. 892411, said 911841 No., and the 991092 No.). The example of desirable methine coloring matter is shown below.

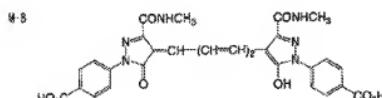
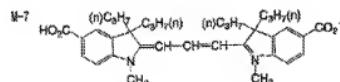
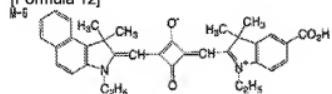
[0096]

[Formula 11]



[0097]

[65] [Formula 12]

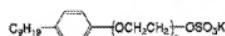


[0098] (iv) In order to make coloring matter stick to the adsorption semiconductor particulate of the coloring matter to a semiconductor particulate, the method of immersing the conductive substrate which has the semiconductor particulate contained layer dry well in the solution of coloring matter, or applying the solution of coloring matter to a semiconductor particulate contained layer can be used. In the case of the former, it is usable in dip coating, a dip method, the roller method, the air knife method, etc. In the case of dip coating, adsorption of coloring matter may be performed at a room temperature, and it may carry out by carrying out heating flowing back as indicated to JP, 7-249790 A. Latter coating methods include the wire bar method, the slide hopper method, the extrusion method, the curtain method, spin method, a spray method, etc. one desirable as a solvent which dissolves coloring matter - alcohols (methanol.) nitril (acetonitrile.), such as ethanol, t-butanol, and benzyl alcohol Nitromethanes, such as propionitrile and 3-methoxy propionitrile, halogenated hydrocarbon (dichloromethane, a dichloroethane, and chloroform.) Ether, such as chlorobenzene (diethylether, tetrahydrofuran, etc.), dimethyl sulfoxide and amide (N,N-dimethylformamide.) N-methyl pyrrolidone, such as N,N-dimethyl acetamido, 1,3-dimethylimidazolidinone, 3-methyl oxazolidinone, ester species (ethyl acetate, butyl acetate, etc.), Carbonic ester, ketone (diethyl carbonate, ethylene carbonate, propylene carbonate, etc.), hydrocarbon (acetone, 2-butanone, cyclohexanone, etc.) (hexane, petroleum ether, benzene, toluene etc.) and these mixed solvents are mentioned.

[0099] As for a porosity semiconductor electrode board, unit surface area ( $1\text{-m}^2$ ) hits, and all the amounts of adsorption of coloring matter have preferred 0.01 - 100mmol. As for the amount of adsorption to a semiconductor particulate of coloring matter, it is preferred that it is the range of per [ semiconductor particulate 1g ] and 0.01 - 1mmol. The sensitization effect in a semiconductor is fully acquired by considering it as the amount of adsorption of such coloring matter. On the other hand, if there is too little coloring matter, the sensitization effect will become insufficient, and if there is too much coloring matter, coloring matter which has not adhered to a semiconductor will float, and it becomes the cause of reducing the sensitization effect. In order to increase the amount of adsorption of coloring matter, heat-treating before adsorption is preferred. After heat-treatment, in order to avoid that water sticks to the semiconductor particulate surface, it is preferred to perform adsorbing operation of coloring matter quickly [ while temperature of a semiconductor electrode board is 60-150  $^{\circ}\text{C}$  ], without returning to ordinary temperature. A colorless compound may be added to coloring matter and coadsorption may be carried out to a semiconductor particulate in order to reduce interactions, such as condensation between coloring matter. An effective compound for this purpose is a compound with surface activity character and structure, for example, the sulfonates like a steroid compound (for example, chenodexycholeic acid) or the following example which have a carboxyl group are mentioned.

[0100]

[Formula 13]



[0101] As for unadsorbed coloring matter, it is preferred that washing removes promptly after adsorption. It is preferred that use a wet cleaning tank and an organic solvent like polar solvents, such as acetonitrile, and an alcohols solvent washes. After adsorbing coloring matter, amines and the 4th class salt may be used and the surface of a semiconductor particulate may be processed. As desirable amines, pyridine, 4-t-butylpyridine, polyvinyl pyridine, etc. are mentioned and TETORO butyl ammonium iodide, tetrahexyl ammonium iodide, etc. are mentioned as the desirable 4th class salt. When these are fluids, it may use as it is, and it may dissolve and use for an organic solvent.

[0102]- A charge transport layer consists of a gel electrolyte which gelled the above-mentioned electrolyte in the optoelectric transducer of charge transport layer-this invention.

[0103]- A counterelectrode (counter electrode) consists of conductive resin mentioned above in the optoelectric transducer of counter electrode-this invention. The conductive resin which may use a thing as shows conductivity by sole resin like poly aniline as conductive resin, and contains a conductive particle and a binder may be sufficient. As a range of desirable surface resistance, it is below 500ohms  $^{\circ}\text{C}$ , and is below 200ohms  $^{\circ}\text{C}$ .

[0104]- Other layers - In order to prevent a short circuit of said counterelectrode (counter electrode) and a conductive substrate, it is preferred to paint a thin film layer of a precise semiconductor as an under coat between a conductive substrate and a photosensitive layer beforehand, and it is effective especially when using an electron transport material and a hole transporting material for a charge transfer layer.  $\text{TiO}_2$ ,  $\text{SnO}_2$ , and  $\text{Fe}_2\text{O}_3$ ,  $\text{WO}_3$ ,  $\text{ZnO}$ , and  $\text{Nb}_2\text{O}_5$  are preferred as said under coat, and it is  $\text{TiO}_2$  still more preferably. An under coat can be painted by a sputtering technique besides the spray pyrolysis method indicated, for example to *Electrochim Acta* 40,643-652 (1995) etc. Desirable thickness of said under coat is 5-1000 nm, and its 10-500 nm is still more preferred.

[0105]-A conductive substrate and a counterelectrode (counter electrode) which act as an electrode -- on the other hand -- or functional layers, such as a protective layer and an antireflection layer, may be provided between both outer surfaces, a conductive layer, and substrates or in the middle of a substrate. According to the construction material, the applying method, vacuum deposition, the sticking method, etc. can be used for formation of these functional layers.

[0106]- It is possible to double with the purpose and to take various gestalten as an internal structure of an example-optoelectric transducer of an internal structure in an optoelectric transducer. If it roughly divides into two, structure which can enter light, and structure which can enter one side to light will be mentioned from both sides. An example of an internal structure of an optoelectric transducer preferably applicable to this invention is shown in drawing 2 - drawing 6.

[0107]Drawing 2 makes the photosensitive layer (semiconductor particulate contained layer) 20 and the gel electrolyte layer (charge transport layer) 30 intervene between the transparent conductive layer 10 and the counter electrode conductive layer (counterelectrode) 40. Drawing 3 forms the metal lead 11 in part on the transparent substrate 50, forms the transparent conductive layer 10 further, and laminates the under coat 60, the gel electrolyte layers (charge transport layer) 30a and 30b of 20 or 2 kinds of photosensitive layers (semiconductor particulate contained layer), and the counter electrode conductive layer (counterelectrode) 40. Drawing 4 forms the conductive layer 10 on the transparent substrate 50, forms the photosensitive layer (semiconductor particulate contained layer) 20 via the under coat 60, laminates two kinds of gel electrolyte layers (charge transport layer) 30a and 30b, and the counter electrode conductive layer (counterelectrode) 40, and forms the metal lead 11 in part on it. Drawing 5 provides a metal lead in part on the counter electrode conductive layer (counterelectrode) 40 of drawing 3. Drawing 6 forms the conductive substrate 70 further on the counter electrode conductive layer (counterelectrode) 40 of drawing 3. All the above-mentioned elements have structure where light enters from the transparent conductive layer 10 side.

[0108](Photoelectric cell) Here, a photoelectric cell of this invention is explained. A photoelectric cell of this invention has an optoelectric transducer of this invention mentioned above. That is, a photoelectric cell of this invention connects with an external circuit via a lead etc., and it is made to make said optoelectric transducer work with external load.

[0109]A case where call a "photoelectrochemical cell" especially a case where a charge transporting material mainly consists of ion transport material among photoelectric cells of this invention, and power generation by sunlight is made into a key objective is called a "solar cell." As for a photoelectric cell of this invention, in order to prevent degradation of a structure and vaporization of contents, it is preferred to seal the side with polymer, adhesives, etc. The external circuit itself connected to a conductive substrate and a counterelectrode (counter electrode) via a lead can use a publicly known thing. When applying an optoelectric transducer of this invention to a photoelectrochemical cell, structure inside the cell is the same as structure of an optoelectric transducer fundamentally mentioned above. The photoelectrochemical cell of this invention can take the fundamentally same modular structure as the conventional solar cell module. Although a cell is constituted on supporting boards, such as metal and ceramics, a solar cell module generally covers an it top with filling resin, cover glass, etc., and structure of incorporating light from an opposite hand of a supporting board is taken. It is also possible to consider it as structure of using transparent materials, such as tempered glass, for a supporting board, constituting a cell and incorporating light from the transparent supporting board side on it. A modular structure specifically called a super straight type, a substrate type, and a potting type, A substrate integral-type modular structure etc. which are used with an amorphous-silicon solar cell etc. are known, and a photoelectrochemical cell can also choose these modular structures suitably with the purpose of use, a service space, and environment. Specifically, it is preferred to use the Japanese-Patent-Application-No. No. 8457 [11 to ] specification with structure of a statement and a mode.

[0110]

[Example]hereafter, this invention is not limited by these examples although an example explains this invention concretely.

[0111]1. Except the production autoclave temperature of titanium dioxide particle content coating liquid having been 230 \*\*, it is a journal OBU American ceramic society of BARUBE and others. It is a method given in 80th volume 3157 page, and the same method, and titanium dioxide concentration obtained the titanium dioxide dispersed matter of 11 mass %. The average size of the obtained titanium dioxide particles was about 10 nm. To this titanium dioxide dispersed matter, it is a polyethylene glycol of 20 mass % to a titanium dioxide. [The molecular weight 20000 and the Wako Pure Chem make] were added, it mixed, and titanium dioxide particle content coating liquid was obtained.

[0112]2. Transparent conductive glass which coated tin oxide which doped production fluoride of titanium dioxide electrode which adsorbed coloring matter [Nippon Sheet Glass Co., Ltd. make and surface resistance to the electric conduction side side of about 10ohm\*\*, and size 2cmx10cm]. Said titanium dioxide particle content coating liquid was applied by a thickness of 120 micrometers with the doctor blade, and after drying for 30 minutes at 25 \*\*, it calcinated for 30 minutes at 450 \*\* with the electric furnace (Yamato Scientific Co., Ltd. make; muffle furnace FP-32 type). The coverage of the titanium dioxide was 18 g/m<sup>2</sup> and thickness was 12 micrometers. As it cooled after the end of calcination and was shown in drawing 7, the glass substrate was cut into 2 cm x a 1.5-cm angle, it left the titanium dioxide film of the 4 mmx4 mm square, and the circumference was shaved off. thus, the processed titanium dioxide electrode was immersed in the adsorption liquid of ruthenium complex coloring matter (\*\*-\*\*-(dithiocyanate)-N,N'-bis(2',2'-bipyridyl 4,4' - dicarboxylic -- acid)ruthenium (II) complex) (R-1) for 16 hours. The solvent of 25 \*\* and adsorption liquid of adsorption temperature is 1:1 (volume ratio) mixture of ethanol and acetonitrile, and concentration of coloring matter was made into 3x10 <sup>-4</sup> mol/L. The titanium dioxide electrode to which coloring matter stuck was dried under the dark place and the nitrogen air current after washing one by one by ethanol and acetonitrile.

[0113]3. Electrolyte (E-1) - (E-12) of the presentation shown in the electrolytic preparation following table 1 was prepared. The structure of the compound used for preparation of an electrolyte was shown below.

[0114]

[Table 1]

電解質組成

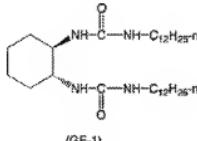
電解質No	電解質組成(質量%)	添加剤
E-1	Y9-1(15), I2(5), Y7(5)/I2(5)	無し
E-2	Y5-1(60)/Y7-2(25)/I2(5)	無し
E-3	Y9-1(15), I2(5), Y7(5)/I2(5)	GE-115
E-4	Y5-1(60)/Y7-2(25)/I2(5)	GE-115
E-5	Y8-1(60)/Y7-2(25)/I2(5)	GE-215
E-6	Y9-1(60)/Y7-2(25)/I2(5)	P-1(5), A-1(5)
E-7	Y8-1(60)/Y7-2(25)/I2(5)	P-2(5), A-1(5)
E-8	Y8-1(60)/Y7-2(25)/I2(5)	P-1(10), A-2(10)
E-9	Y8-1(60)/Y7-3(15)/I2(5)	P-3(5), A-3(5)
E-10	Y8-1(60)/Y7-2(25)/I2(5)	M-1(10), S-1(5)
E-11	Y8-1(60)/Y7-2(25)/I2(5)	アルカリ性セイ
E-12	Y8-1(30)/Y7-2(25)/I2(5)	グリコ

[1] 平均粒子径約1.8μm

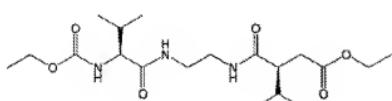
[2] 平均粒子径約1.2μm

[0115]

[Formula 14]



特開2000-58140号公報の(I-5)

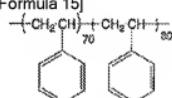


(GE-2)

特開2000-58140号公報の(I-7)

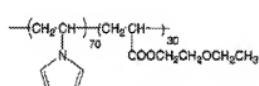
[0116]

[Formula 15]



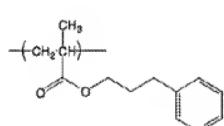
(P-1)

特開2000-86724号公報の1-1



(P-2)

特開2000-86724号公報の1-19



(P-3)

特開2000-35550号公報の2-38

[0117]

[Formula 16]



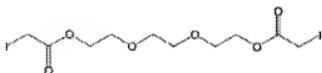
(A-1)



(A-2)

特開2000-88724号公報の2-3

特開2000-88724号公報の2-11



(A-3)

特開2000-35050号公報の1-2

[0118]4. Produced by production 2. of the cell C-1-5 for production (1) comparison of an optoelectric transducer. The platinum vacuum evaporation glass substrate (2 cm x 1.5 cm) in which a 25-micrometer heat contraction nature resin sheet (Du Pont make; trade name FUSABOND) as shown by drawing 7 was stuck on the titanium dioxide electrode (2 cm x 1.5 cm) by which color sensitizing was carried out is piled up as a counter electrode (counterelectrode). Putting a pressure on a thickness direction mechanically, it heated for 20 seconds at 130 \*\*, and the spacer was made to dissolve and stick by pressure.

[0119](1-a) From the spacer opening of the element assembled by the production above of the cell C-1 for comparison, said electrolyte E-1 was infiltrated, except for the outermost terminal area circumference, the seal of the circumference of a cell was carried out, it was hardened with epoxy adhesive, and the cell C-1 for comparison was produced.

[0120](1-b) After pouring it in, keeping the electrolyte E-2 at 50 \*\* and filling inter-electrode with an electrolysis solution from the spacer opening of the element assembled by the production above of the cell C-2 for comparison, the cell was attracted under the vacuum for several hours, and the inside of a cell including a coloring matter adsorption titanium dioxide porous electrode and an electrolyte was deaerated. Except for the outermost terminal area circumference, the seal of the circumference of a cell was carried out to the last, it was hardened with epoxy adhesive at it, and the cell C-2 for comparison was produced.

[0121](1-c) In production of the cell C-1 for the production aforementioned comparison of the cell C-3 for comparison, instead of the electrolyte E-1, it is the same method as the cell C-1 for comparison, and the cell C-3 for comparison was produced except the point using the electrolyte E-3 heated at 80 \*\*.

[0122](1-d) In production of the cell C-2 for the production aforementioned comparison of the cell C-4 for comparison, instead of the electrolyte E-2, it is the same method as the cell C-2 for comparison, and the cell C-4 for comparison was produced except the point using the electrolyte E-4 heated at 80 \*\*.

[0123](1-e) In production of the cell C-2 for the production aforementioned comparison of the cell C-5 for comparison, After pouring in and carrying out the seal of the electrolyte E-6 instead of the electrolyte E-2, except the point heated at 80 \*\* for 5 hours in order to gel the poured-in electrolyte, it is the same method as the cell C-2 for comparison, and the cell C-5 for comparison was produced.

[0124](2-a) As the production (2-a) cell C-6 of the cell C-6-16 of this invention and production drawing 8 of C-7 show, Around [a titanium dioxide film] the titanium dioxide electrode (2 cm x 1.5 cm) which was produced by 2. and by which color sensitizing was carried out, A 25-micrometer heat contraction nature resin sheet (Du Pont make; trade name FUSABOND) was stuck, and the electrolyte E-4 heated at 80 \*\* on the titanium dioxide film was applied so that a titanium dioxide film might be covered, and it was neglected at 80 \*\* for 3 hours. When it cooled to the room temperature after that, the electrolyte E-4 was gelled. Thus, on the gelled electrolyte, carbon paste (FUJIKURA KASEI CO., LTD. make; dotite) was applied and dried, and the cell C-6 was produced. In production of said cell C-6, instead of the electrolyte E-4, it is the same method as the cell C-6, and the cell C-7 was produced except the point of having used the electrolyte E-5.

[0125](2-b) The electrolyte E-6 heated to 50 \*\* of production of the cell C-8-11 was applied so that a titanium dioxide film might be covered, and it was deaerated every 8 hours under the vacuum. Then, it heated at 80 \*\* among dry air (dew point-60 \*\*) for 3 hours, and the electrolyte was gelled. On this gel electrolyte, carbon paste (FUJIKURA KASEI CO., LTD. make; dotite) was applied and dried, and the cell C-8 was produced. In production of said cell C-8, instead of the electrolyte E-6, it is the same method as said cell C-8, and the cell C-9, and 10 and 11 were produced, respectively except the electrolyte E-7 and the point of having used 9 and 10, respectively.

[0126](2-c) The electrolyte E-6 heated to 50 \*\* of production of the cell C-12-14 was applied so that a titanium dioxide film might be covered, and it was deaerated every 8 hours under the vacuum. Then, it heated at 80 \*\* for 3 hours, and the electrolyte was gelled. The electrolyte E-6 and the gel electrolyte of E-8 were laminated by applying the electrolyte E-8, heating at 80 \*\* further, for 3 hours, and gelling E-8 on this gel electrolyte. Besides, further, carbon paste (FUJIKURA KASEI CO., LTD. make; dotite) was applied and dried, and the cell C-12 was produced. In production of said cell C-12, respectively, it is the point of having changed into E-11 and E-12 the electrolyte painted on the gel of the electrolyte E-6, respectively, it is the same method as the cell C-12, and the cell C-13 and C-14 were produced.

[0127](2-d) In production of the cell C-15 and the production aforementioned cell C-8 of 16, instead of using carbon paste as counter electrode conductive resin -- a graphite paste (graphite.) The epoxy resin and the hardening agent were kneaded, except the point using the thing diluted with toluene, and the platinum black paste (what kneaded graphite, the epoxy resin, and the hardening agent, and was diluted with toluene) respectively, it is the same method as said cell C-8, and the cell C-15 and C-16 were produced, respectively.

[0128]Production of the above-mentioned cell was performed as much as possible in dew point-60 \*\* dry air. Thus, the electrolyte of a cell and the combination of a counterelectrode which were produced were shown in the following table 2.

[0129]

[Table 2]

電池No.	電解質	封肉系種
C-1	E-1(溶媒)	白金蒸着ガラス
C-2	E-2(溶媒)	白金蒸着ガラス
C-3	E-3(溶媒)ゲル	白金蒸着ガラス
C-4	E-4(溶媒)ゲル	白金蒸着ガラス
C-5	E-5(溶媒)ゲル	白金蒸着ガラス
C-6	E-4(溶媒)ゲル	カーボンベースト
C-7	E-5(溶媒)ゲル	カーボンベースト
C-8	E-5(溶媒)ゲル	カーボンベースト
C-9	E-7(溶媒)ゲル	カーボンベースト
C-10	E-9(溶媒)ゲル	カーボンベースト
C-11	E-10(溶媒)ゲル	カーボンベースト
C-12	E-6(溶媒)ゲル	カーボンベースト
C-13	E-6(溶媒)ゲル E-11(溶媒)ゲル	カーボンベースト
C-14	E-6(溶媒)ゲル E-12(溶媒)ゲル	カーボンベースト
C-15	E-6(溶媒)ゲル	グラファイトベースト
C-16	E-6(溶媒)ゲル	白金蒸着ベースト

[0130]5. By letting a spectrum filter (AM1.5 by Oriel) pass for the light of the xenon lamp (made by USHIO, INC.) of the measurement 500W about photoelectric conversion efficiency and endurance, imitation sunlight was generated and this light intensity was adjusted to 10 mW/cm<sup>2</sup> in the vertical plane. Silver paste was applied to the end of the electrically conductive glass of an optoelectric transducer, it was considered as the negative electrode, and this negative electrode and counter electrode (anode) were connected to the current potential measuring device (case rhe SMU238 type). Irradiating with imitation sunlight vertically, the current potential characteristic was measured and conversion efficiency was searched for. The J<sub>sc</sub> decreasing rate after 30 \*\* and 300-hour temporality was shown with the conversion efficiency of the produced optoelectric transducer in the following table 3 about the produced cell.

[0131]

[Table 3]

電池No.	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF	η (%)	J <sub>sc</sub> 低下率 (%)	備考
C-1	0.95	0.67	0.64	3.71	96	比較例
C-2	0.80	0.59	0.62	3.93	6	比較例
C-3	0.80	0.64	0.68	3.92	92	比較例
C-4	0.88	0.62	0.68	2.27	11	比較例
C-5	0.63	0.59	0.61	2.27	14	比較例
C-6	0.81	0.62	0.66	3.41	4	本発明
C-7	0.85	0.69	0.69	3.81	2	本発明
C-8	0.86	0.81	0.67	3.53	7	本発明
C-9	0.80	0.67	0.68	2.42	6	本発明
C-10	0.86	0.60	0.66	3.41	8	本発明
C-11	0.91	0.62	0.65	3.67	7	本発明
C-12	0.86	0.63	0.63	3.42	8	本発明
C-13	0.67	0.59	0.63	3.20	6	本発明
C-14	0.84	0.69	0.63	2.23	4	本発明
C-15	0.88	0.62	0.68	3.63	7	本発明
C-16	0.85	0.62	0.69	3.76	8	本発明

J<sub>sc</sub>:短路電流密度, V<sub>oc</sub>:開路電圧, FF: 形状因数, η: 変換効率

J<sub>sc</sub>低下率: (電池を30°Cで360時間経過した後のJ<sub>sc</sub>) / (作成直後のJ<sub>sc</sub>) × 100

[0132]It was checked that the optoelectric transducer used for the photoelectric cell of this invention shows high conversion efficiency and endurance from said table 3 compared with the optoelectric transducer used for the cell for comparison. As stated with the manufacturing method, the complicated work of pouring an electrolysis solution into the narrow space of a working pole and a counter electrode was unnecessary, and could laminate by spreading to the counter electrode, and it turned out that the producing method is easier than the conventional cell.

[0133]

[Effect of the Invention]According to this invention, it has practical production aptitude, and it is cheap, and excels in conversion efficiency and endurance, and the photoelectric cell using an optoelectric transducer using the semiconductor

particulate by which sensitization was carried out with coloring matter, a manufacturing method for the same, and this optoelectric transducer can be provided.

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[Translation done.]

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2.\*\*\*\* shows the word which can not be translated.

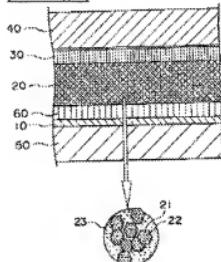
3.In the drawings, any words are not translated.

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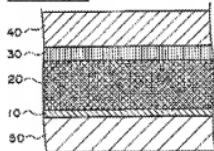
DRAWINGS

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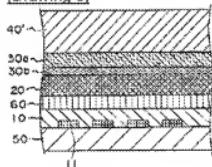
[Drawing 1]



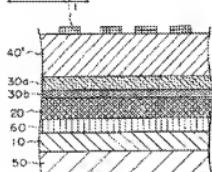
[Drawing 2]



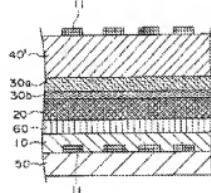
[Drawing 3]



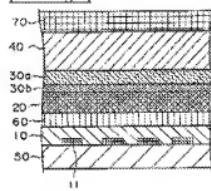
[Drawing 4]



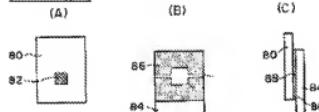
[Drawing 5]



### [Drawing 6]



[Drawing 7]



[Drawing 8]



[Translation done.]